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Why can the Diels–Alder reaction of 9,10-diphenylanthracene with 4-phenyl-1,2,4-triazoline-3.5-dione pass by an abnormal way?

Vladimir D. Kiselev,* Ilzida I. Shakirova, Elena A. Kashaeva, Lyubov N. Potapova, Dmitry A. Kornilov, Dmitry B. Krivolapov and Alexander I. Konovalov

A. M. Butlerov Institute of Chemistry, Kazan (Volga Region) Federal University, 420008 Kazan, Russian Federation. Fax: +7 843 292 7278; e-mail: vkiselev.ksu@gmail.com

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9,10-Diphenylanthracene reacts with dienophile by 1,4-positions rather than 9,10-ones of trivial anthracenes, that has been justified with estimation of kinetic and thermodynamic parameters of the process.

4-Phenyl-1,2,4-triazoline-3,5-dione exhibits the highest reactivity in the Diels–Alder reaction with dienes, as compared with other dienophiles.[1–3] For fifteen dienes, the rate constants and enthalpies of reactions with 4-phenyl-1,2,4-triazoline-3,5-dione, tetracyanoethylene and maleic anhydride were compared.[4] From these data, it follows that the activity of 4-phenyl-1,2,4-triazoline-3,5-dione is higher than that of maleic anhydride by five or six orders of magnitude.

We studied the reaction rate of a very inactive diene, 9,10-diphenylanthracene **1a**, with the most active dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione **2**, in a toluene solution at 5–45 °C and 1–2126 bar (Scheme 1). The enthalpy, entropy, activation volume, reaction volume and the structure of adduct **3a** were determined.

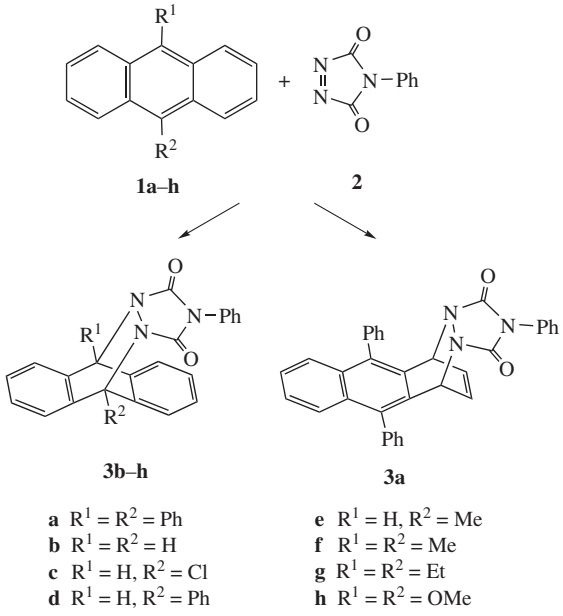
The overlapping of the 1,8-hydrogen atoms of the anthracene moiety and 2,6-hydrogen atoms of the phenyl group in 9-phenylanthracene **1d** leads to a dihedral angle of about 60° between these fragments.[5] For 9,10-diphenylantracene **1a**, the almost orthogonal planes of phenyl groups to the anthracene plane were observed.[6] The rate constant of the Diels–Alder reaction with the C=C bonds can be estimated[7] from the equation

$$\log k_2 = -28.81 + 316.3/(IP - EA) - 0.699R_{C(1)-C(4)}/(IP - EA) - 0.054\Delta_r H,\ r = 0.972 \quad (1)$$

Here the value of k_2 is in dm^3 mol^{-1} s^{-1}, the ionization potential (*IP*) and electron affinity (*EA*) are in eV, $R_{C(1)-C(4)}$ is in pm, the enthalpy of reaction, $\Delta_r H$, is in kJ mol^{-1}, and *r* is the correlation coefficient.

The rate of reaction of 9-phenylanthracene **1d** with maleic anhydride in toluene at 25 °C (3.6×10^{-7} dm^3 mol^{-1} s^{-1}) is 2.5 orders of magnitude lower than that predicted from equation (1).[7] In the absence of steric hindrances, the relative activity of the cycloaddition reaction on 9,10- and 1,4-atoms of anthracene can be estimated using equation (1). The required parameters are available in the literature.[8–10]

From these data, it follows that the difference in the heats of hydrogenation of 9,10- and 1,4-anthracene atoms is –65±8 kJ mol^{-1}. This corresponds [equation (1)] to a $k_{(9,10)}/k_{(1,4)}$ ratio of 3200. For a series of linear acenes, the activity of different cycles in the Diels–Alder reaction with acetylene has been calculated,[11] which implies the ratio $k_{(9,10)}/k_{(1,4)} = 3500$. The reaction of substituted anthracenes **1b–h** with dienophile **2** runs at the most active *meso*-position of the diene to form adducts **3b–h**.[1–4] It is clear that, for a sterically shielded and inaccessible 9,10-reaction centre of diene **1a**, the Diels–Alder reaction is impossible regardless of the potential dienophile activity. Under normal conditions, the reaction between diene **1a** and all known dienophiles with C=C bonds does not take place, whereas in case of dienophile **2** it occurs even at room temperature ($k_2 = 2.7\times10^{-3}$ dm^3 mol^{-1} s^{-1}, toluene, 25 °C). From the obtained values of $k_{(9,10)}/k_{(1,4)}$ it follows that when the investment of energy required for the flattening of diene **1a** is more than 20 kJ mol^{-1}, the direction of cycloaddition can be changed to less active but sterically accessible 1,4-atoms of anthracene.



a $R^1 = R^2 = Ph$
b $R^1 = R^2 = H$
c $R^1 = H$, $R^2 = Cl$
d $R^1 = H$, $R^2 = Ph$
e $R^1 = H$, $R^2 = Me$
f $R^1 = R^2 = Me$
g $R^1 = R^2 = Et$
h $R^1 = R^2 = OMe$

Scheme 1

The ^{1}H NMR spectrum (Figure 1) of adduct **3a** {400 MHz, $CDCl_3$, 25 °C, δ: 5.92 [t, C(1)H, C(12)H], 6.87 [t, =C(18)H, =C(19)H], atom numeration as in Figure 2} is very different from the spectra of adducts **3b–h**. The presence of two protons at the saturated carbon atoms C(1) and C(12) and the ethylene fragment =C(18)H, =C(19)H is consistent with the formation of 1,4-adduct **3a**, which is not observed in the spectrum of adduct **3f** (Figure 1). Additionally, X-ray analysis (Figure 2)† confirms the formation of the *exo*-conformation of adduct **3a** – 3,10,15-triphenyl-13,15,17-triazapentacyclo[10.5.2.0^{2,11}.0^{4,9}.0^{13,17}]-nonadeca-2,4(9),5,7,10,18-hexaene-14,16-dione. The formation of *endo*-isomer may inhibit 9,10-phenyl substituents.

Note that the ^{1}H NMR spectrum of **3a** is identical to that reported elsewhere,[12] but the possible formation of such adduct was not considered.